Common Approach to Obtaining Experimental Data for Developing Predictive NOx Adsorber Models

Neal Currier, Bill Epling

Cummins, Inc.

Diesel Exhaust Emissions Reduction Conference

Common Approach

Standardize the experimental work required to develop/refine models of NOx adsorber catalyst devices

- Ability to evaluate multiple formulation
- Obtain information that is common across multiple suppliers
- Standardize the model development/tuning procedures
- Assure completeness of the device description

Goals

- Behavior that needs to be captured
  - Functions of
    - Temperature
    - Reductant Amount
    - Reductant Type
    - Flow rate (space velocity)
    - NO – NO_2 in slip and regeneration products
    - Cycle behavior
- Characterize distinct features resulting from complex behavior
  - Transient nature of the device, engine, controls drive the need to truly understand:
    - the reaction and surface chemistry in most of its complexity,
    - fluid mechanics,
    - and heat and mass transfer of the catalyst

CLEERS LNT Focus Group

Develop protocol for collecting data descriptive of catalyst behavior

- Cover a broad operating space
- Cover all major features of the catalyst behavior
- Require only commonly available laboratory equipment
- Require less than two weeks to complete
- Be applicable to a wide variety of catalyst formulations
- Provide data that would, at least, adequately test model performance

Not designed to provide mechanistic information

To date – define a minimal data set and the protocol for obtaining these data

The CLEERS Protocol

Short cycle testing –

Describe catalyst behavior in an operational environment

Long cycle testing –

Describe catalyst behavior close to saturation

Run No.	Temp (deg C)+	Gas Mix++	SV (1/hr)	Lean period (s)	Reductant*	Regen peak (ppm)**	Regen period (s)#	No. of cycles
1	550	1	30,000	0	H2	1,000	900	1
2	550	2	30,000	60	CO/H2	1.8%	5	30
3	550	2	30,000	60	CO/H2	0.9%	5	30
4	550	1	30,000	0	H2	1,000	900	1
5	463	2	30,000	60	CO/H2	1.8%	5	30
6	463	2	30,000	60	CO/H2	0.9%	5	30
7	550	1	30,000	0	H2	1,000	900	1
8	375	2	30,000	60	CO/H2	1.8%	5	30
9	375	2	30,000	60	CO/H2	0.9%	5	30
10	550	1	30,000	0	H2	1,000	900	1
11	288	2	30,000	60	CO/H2	1.8%	5	30
12	288	2	30,000	60	CO/H2	0.9%	5	30
13	550	1	30,000	0	H2	1,000	900	1
14	200	2	30,000	60	CO/H2	1.8%	5	30
15	200	2	30,000	60	CO/H2	0.9%	5	30
16	550	1	30,000	0	H2	1,000	900	1
17	375	2	15,000	60	CO/H2	1.8%	5	30
18	550	1	30,000	0	H2	1,000	900	1
19	375	2	50,000	60	CO/H2	1.8%	5	30

Allow adequate flexibility to cover catalysts designed for different applications

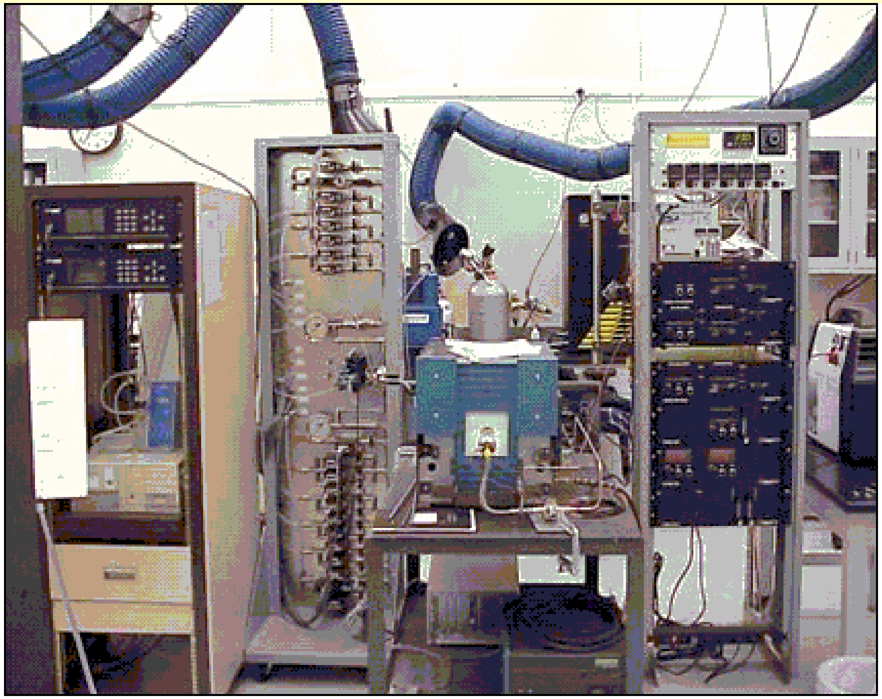
Focus on device level behavior – account for non-catalyst features, *e.g.* substrate

Cycle Summaries

- Short Cycle
  - Clean the sample at 550°C, H_2 reductant, 10 minutes
  - Cool to appropriate T
  - 60 seconds lean, 5 seconds rich
    - Reductant level described as 2X stored NO_X, used 2x entering NO_X
  - 30 cycles at this reductant level
  - At end of 30th cycle, switch reductant level to 1x entering NO_X
  - 30 cycles
  - Heat to 550°C, clean
- Long Cycle
  - Cleaning – same as short cycle
  - Cool to appropriate T
  - 15 minutes lean, 10 minutes rich
  - Repeat cycles
  - Reductant level set at 1000 ppm
    - For HC reductant, 1000 ppm H_2 equivalent
- OSC measurement

Expetimental

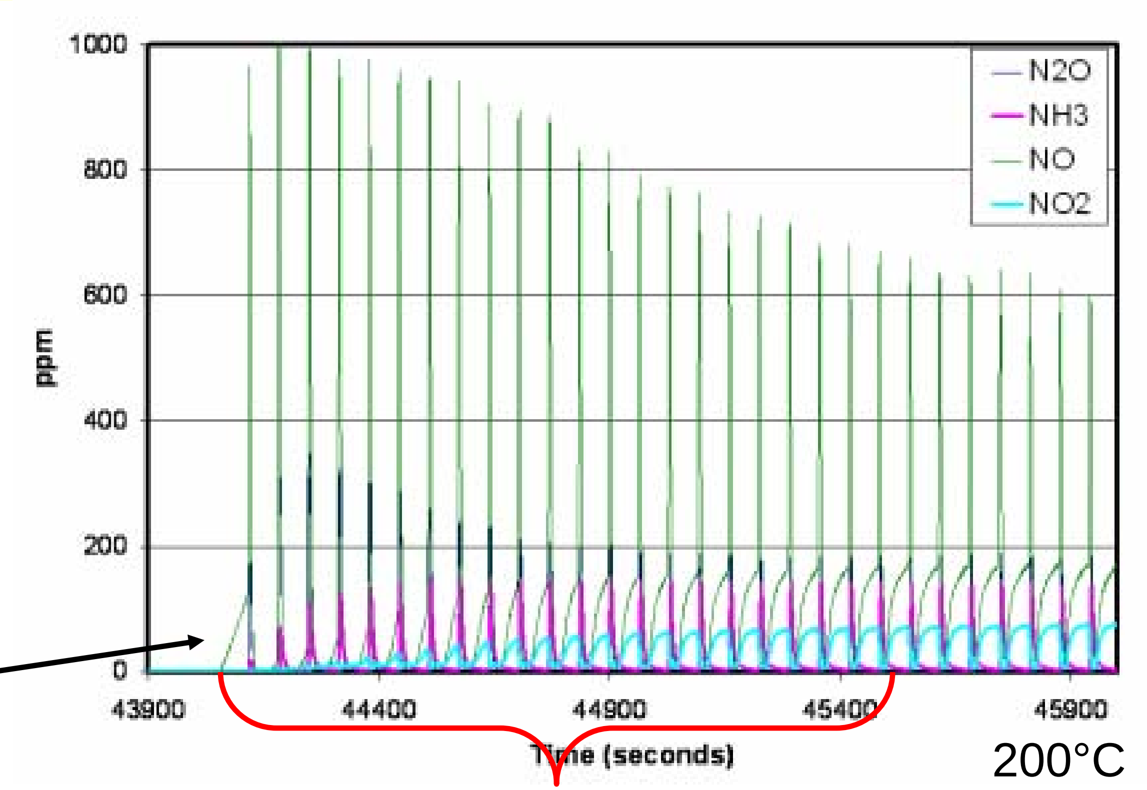
- Reactor - Cummins' automated pilot scale catalyst reactor
- ~ 1 week to execute the protocol
- Instrumentation -
  - FTIR, UEGO, & NOx sensors
  - IR - 2 Hz, sensors - as high as 10 Hz
- CLEERS LNT standard sample aged at NTRC



Typical Short Cycle

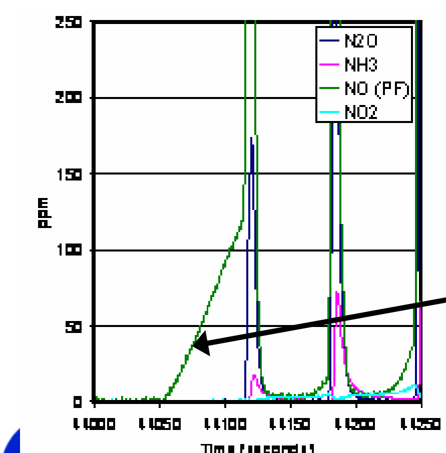
Shows transient effects at several scales

Reaches stable cycle for several cycles



200°C

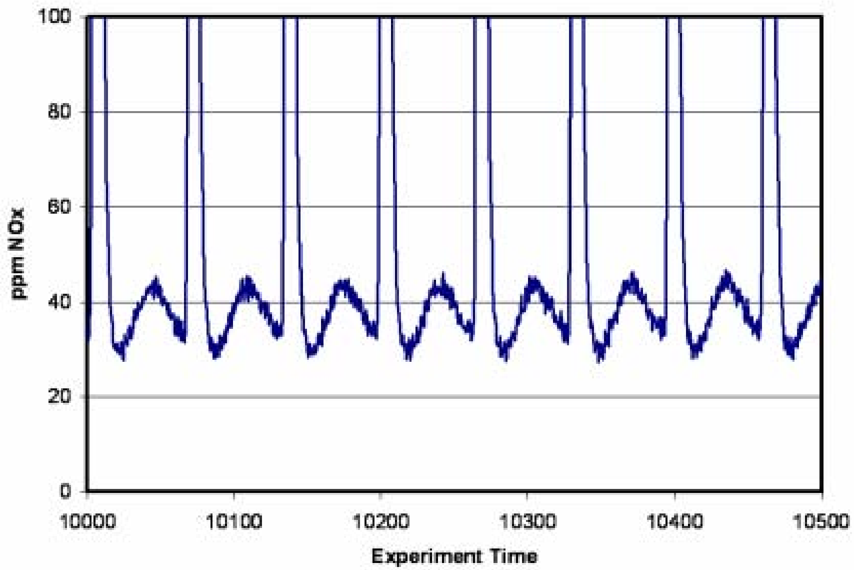
22 cycles → SS?



"Pretreated" surface leads to different trapping profile

Non-catalytic Features

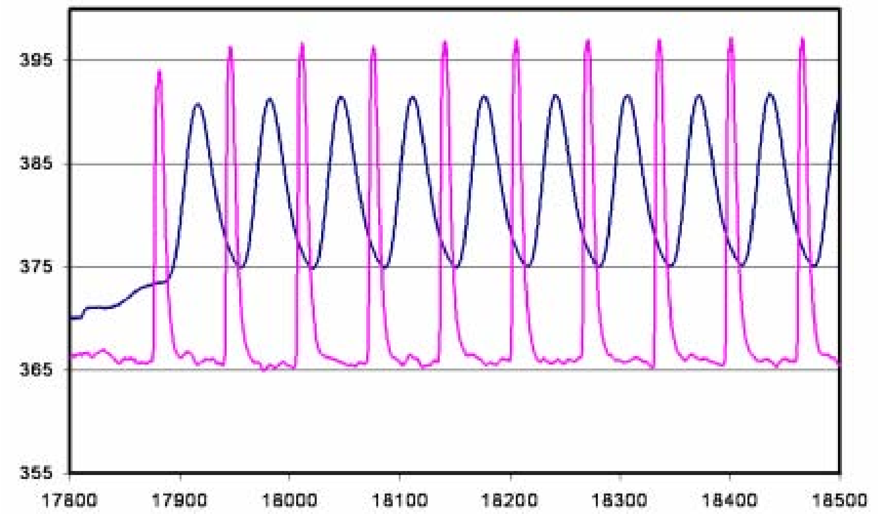
Total NO_X ($NO + NO_2$)



Total NO_X shows change in trapping during lean

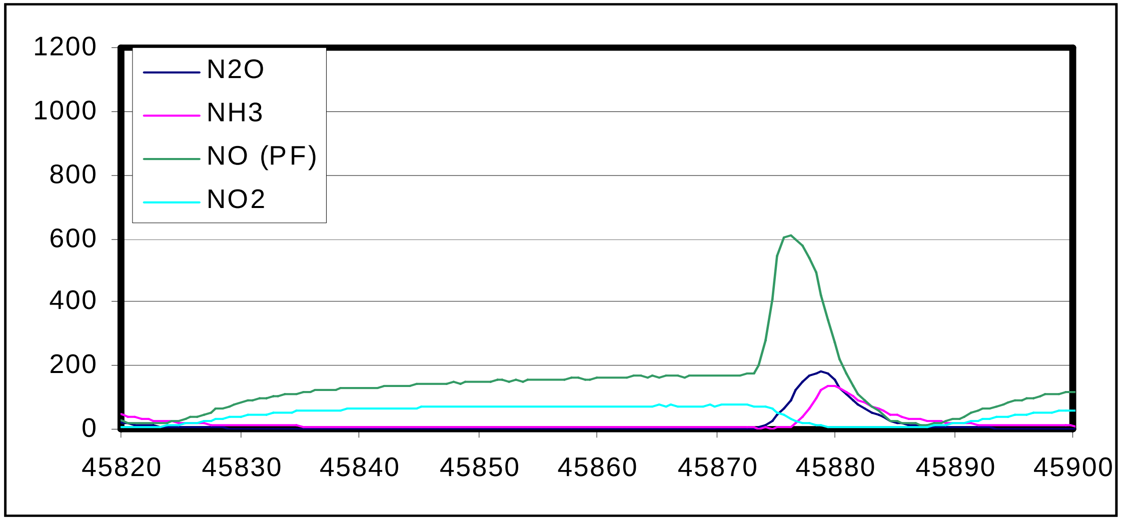
Temperature wave traverses catalyst length (phase shift)

Trapping efficiency or oxidation?



Chemistry of the model only works if thermal model is right

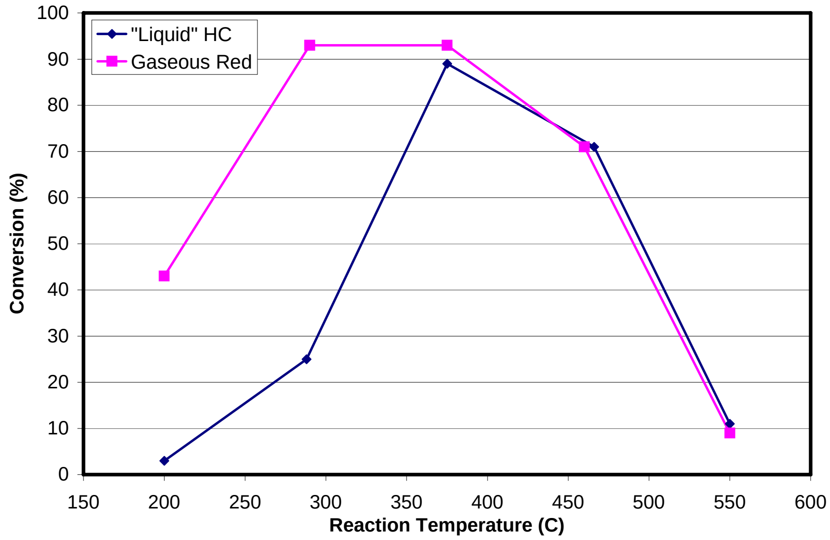
N species release sequence

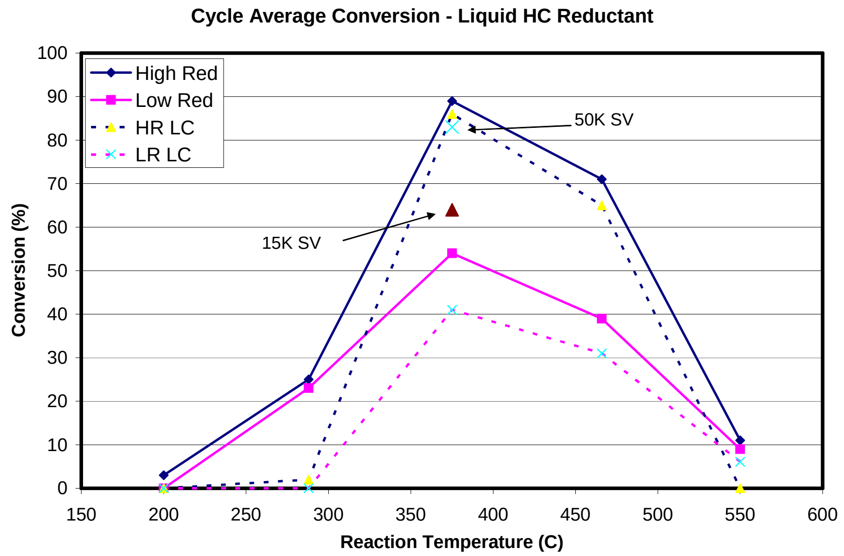


200°C Test (all species observed)

- NO_2 ~ NO → N_2O → NH_3 at 200°C (at higher T, difficult to resolve differences between NO, NO_2 and N_2O)
- Is it less NO_X, degree of surface reduction; different NOx storage sites; surface residence time?

Reductant and Space Velocity Effects





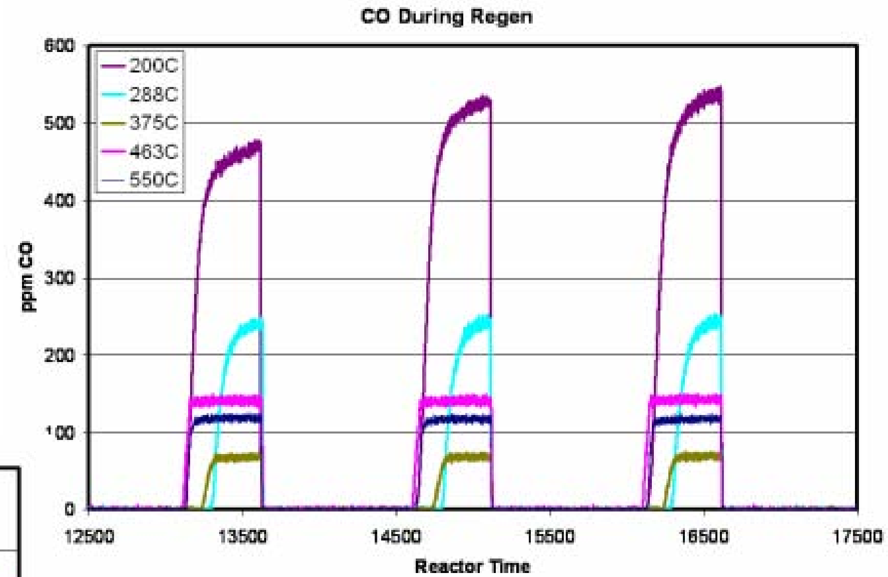
Impact of reductant type is clear at low temperatures where reforming reactions are limiting

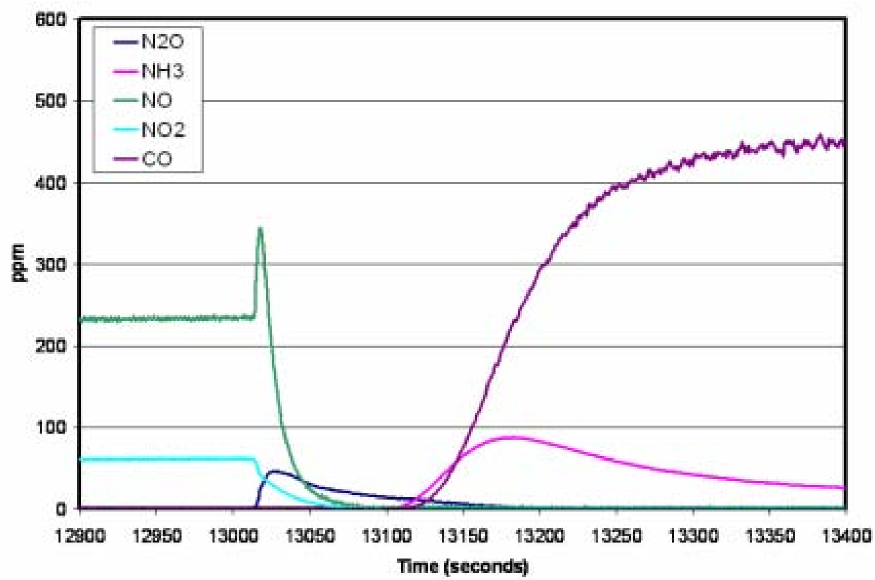
Impact of space velocity is the result of reductant mass flux

Cycle average changes with time

Long Cycle

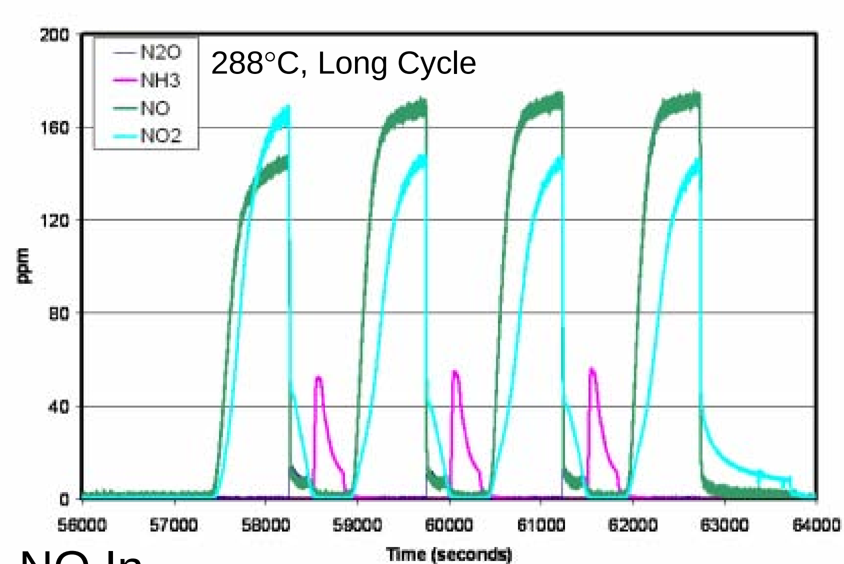
- Some integral device effects can be probed with the long cycle – e.g. regen product sequencing and split



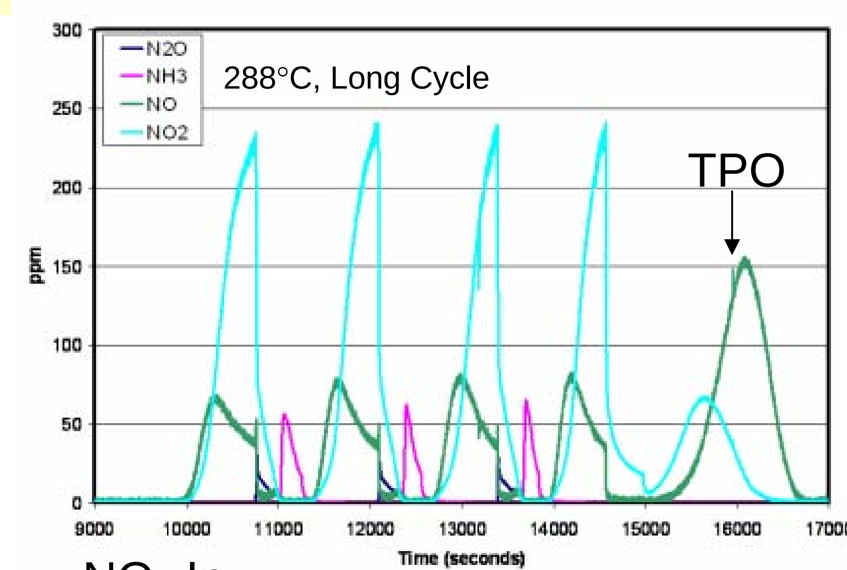


- With higher NOx loadings, reductant usage is highlighted
- Differences based on reductant and temperature

The Protocol is not Exhaustive



NO In



NO_2 In

- 50% more NOx adsorbed with NO_2
- Disproportionation mechanism more evident with NO_2
  - The additional data allows provides more mechanistic information – disproportionation, NO_2 versus O_2 as oxidant
  - Would increase experimental cost

Summary

- A relatively simple suite of testing generates a rich set data demonstrating a wide range of catalyst device behaviors
- Using only these data for model building may be challenging
- These data can be useful for model tuning and validation
- Lab to lab repeatability remains to be established

Acknowledgements

- US DOE, Office of FreedomCar and Vehicle Technologies
- CLEERS LNT Focus Group
- Jim Lucas, Heather Eadler
  - Assistance with data collection